

# CW HI Laser Based on a Stationary Inverted Lyman Population Formed from Incandescently Heated Hydrogen Gas with Certain Group I Catalysts

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## ABSTRACT

Each of the ionization of  $Rb^+$  and cesium and an electron transfer between two  $K^+$  ions ( $K^+ / K^+$ ) provide a reaction with a net enthalpy of an integer multiple of the potential energy of atomic hydrogen, 27.2 eV. The corresponding Group I nitrates provide these reactants as volatilized ions directly or as atoms by undergoing decomposition or reduction to the corresponding metal. The presence of each of the reactants identified as providing an enthalpy of 27.2 eV formed a low applied temperature, extremely low voltage plasma called a resonance transfer or rt-plasma having strong vacuum ultraviolet (VUV) emission. In contrast, magnesium and aluminum atoms or ions do not ionize at integer multiples of the potential energy of atomic hydrogen.  $Mg(NO_3)_2$  or  $Al(NO_3)_3$  did not form a plasma and caused no emission.

For further characterization, we recorded the width of the 6563 Å Balmer  $\alpha$  line on light emitted from rt-plasmas. Significant line broadening of 18, 12, and 12 eV was observed from a rt-plasma of hydrogen with  $KNO_3$ ,  $RbNO_3$ , and  $CsNO_3$ , respectively, compared to 3 eV from a hydrogen microwave plasma. These results could not be explained by Stark or thermal broadening or electric field acceleration of charged species since the measured field of the incandescent heater was extremely weak, 1 V/cm, corresponding to a broadening of much less than 1 eV. Rather the source of the excessive line broadening is consistent with that of the observed VUV emission, an energetic reaction caused by a resonance energy transfer between hydrogen atoms and  $K^+ / K^+$ ,  $Rb^+$ , and cesium, which serve as catalysts.

$KNO_3$  and  $RbNO_3$  formed the most intense plasma. Remarkably, a stationary inverted Lyman population was observed in the case of an rt-plasma formed with potassium and rubidium catalysts. These catalytic reactions may pump a cw HI laser as predicted by a collisional radiative model used to determine that the observed overpopulation was above threshold.

## 1. Introduction

The Lyman  $\alpha$ ,  $\beta$ , and  $\gamma$  lines of atomic hydrogen at 121.6 nm, 102.6 nm, and 97.3 nm in the vacuum ultraviolet (VUV) region are due to the transitions from  $n=2$ ,  $n=3$ , and  $n=4$  to  $n=1$ , respectively. These lines are of great importance in many applications ranging from photochemistry, to laboratory simulations of planetary atmospheres, to astrophysics and plasma physics. In plasma physics, the Lyman series line intensities and their ratios are frequently used in the determination of plasma parameters such as hydrogen number densities and other quantities such as particle fluxes or ion recombination processes [1-2]. For the last four decades, scientist from academia and industry have been searching for lasers using hydrogen plasma [3-6]. Developed sources that provide a usefully intense hydrogen plasma are high powered lasers, arcs and high voltage DC and RF discharges, synchrotron devices, inductively coupled plasma generators, and magnetically confined plasmas. However, the generation of population inversion is very difficult. Recombining expanding plasmas jets formed by methods such as arcs or pulsed discharges is considered one of the most promising methods of realizing an HI laser.

It was reported previously that a new plasma source has been developed that operates by incandescently heating a hydrogen dissociator to provide atomic hydrogen and heats a catalyst such that it becomes gaseous and reacts with the atomic hydrogen to produce a plasma called a resonance transfer or rt-plasma. It was extraordinary, that intense VUV emission was observed by Mills et al. [7-8] at low temperatures (e.g.  $\approx 10^3$  K) and an extraordinary low field strength of about 1-2 V/cm from atomic hydrogen and certain atomized elements or certain gaseous ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV. The theory was given previously [9-11].

The Group I and Group VIII elements are unique in that, with the exception of xenon, atoms and or ions from these groups provide a reaction with a net enthalpy that is a close match to an integer multiple of the potential energy of atomic hydrogen,  $m \cdot 27.2$  eV where  $m$  is an integer. The corresponding reactions of Group I elements with a net

enthalpy of  $m \cdot 27.2 \text{ eV}$  which are proposed to form an rt-plasma follow:

The first and second ionization energies of lithium are  $5.39172 \text{ eV}$  and  $75.6402 \text{ eV}$ , respectively [12]. The double ionization reaction of  $\text{Li}$  to  $\text{Li}^{2+}$ , then, has a net enthalpy of reaction of  $81.032 \text{ eV}$ , which is equivalent to  $m = 3$ .

The second, third, and fourth ionization energies of sodium are  $47.2864 \text{ eV}$ ,  $71.6200 \text{ eV}$ , and  $98.91 \text{ eV}$ , respectively [12]. The triple ionization reaction of  $\text{Na}^+$  to  $\text{Na}^{4+}$ , then, has a net enthalpy of reaction of  $217.8164 \text{ eV}$ , which is equivalent to  $m = 8$ .

The second ionization energy of potassium is  $31.63 \text{ eV}$ , and  $\text{K}^+$  releases  $4.34 \text{ eV}$  when it is reduced to  $\text{K}$  [12]. The combination of reactions  $\text{K}^+$  to  $\text{K}^{2+}$  and  $\text{K}^+$  to  $\text{K}$ , then, has a net enthalpy of reaction of  $27.28 \text{ eV}$ , which is equivalent to  $m = 1$ . Also, the first, second, and third ionization energies of potassium are  $4.34066 \text{ eV}$ ,  $31.63 \text{ eV}$ , and  $45.806 \text{ eV}$ , respectively [12]. The triple ionization reaction of  $\text{K}$  to  $\text{K}^{3+}$ , then, has a net enthalpy of reaction of  $81.7766 \text{ eV}$ , which is equivalent to  $m = 3$ .

The second ionization energy of rubidium is  $27.28 \text{ eV}$  [12]; thus, the reaction  $\text{Rb}^+$  to  $\text{Rb}^{2+}$  has a net enthalpy of reaction of  $27.28 \text{ eV}$ , which is equivalent to  $m = 1$ .

The first and second ionization energies of cesium are  $3.89390 \text{ eV}$  and  $23.15745 \text{ eV}$ , respectively [12]. The double ionization reaction of  $\text{Cs}$  to  $\text{Cs}^{2+}$ , then, has a net enthalpy of reaction of  $27.05135 \text{ eV}$ , which is equivalent to  $m = 1$ .

Rt-plasmas with Group I catalysts were reported previously [7]. In this paper, we report on further characterization of rt-plasmas with Group I catalysts wherein  $m = 1$ . Group I nitrates were used since they are volatile at relatively low temperatures and also undergo hydrogen reduction and gradual thermal decomposition. Thus, they provide gaseous ions  $M^+$  or atoms  $M$ .

The energetic hydrogen atom densities and energies were calculated from the width of the  $6563 \text{ \AA}$  Balmer  $\alpha$  line emitted from a control hydrogen microwave plasma and rt-plasmas. The characteristic emission from the catalyst was measured.  $\text{KNO}_3$  and  $\text{RbNO}_3$  formed the most intense plasmas. Remarkably, the population of the levels  $n = 3$  and  $n = 4$  of hydrogen were continuously inverted with respect to  $n = 2$  in an rt-plasma formed with the  $\text{K}^+$  and  $\text{Rb}^+$  catalysts. To our knowledge, this

is the first report of population inversion in a chemically generated plasma. The plasma was further characterized by measuring the electron temperature  $T_e$  from intensity ratios of alkali lines.

## 2. Experimental

The VUV spectrum (900–1300 Å), the width of the 6563 Å Balmer  $\alpha$  line, and the high resolution visible spectrum were recorded on light emitted from a hydrogen microwave discharge performed according to methods reported previously [13-14] that served as a control for measurements recorded on light emitted from rt-plasmas of hydrogen with  $KNO_3$ ,  $RbNO_3$ , or  $CsNO_3$ . The experimental set up described previously [7-8] and shown in Figure 1 comprised a thermally insulated quartz cell with a cap that incorporated ports for gas inlet, outlet, and photon detection. A tungsten filament heater and hydrogen dissociator were in the quartz tube as well as a cylindrical titanium screen that served as a second hydrogen dissociator that was coated with catalysts  $KNO_3$ ,  $RbNO_3$ , or  $CsNO_3$  and control materials  $Mg(NO_3)_2$  or  $Al(NO_3)_3$ . The titanium screen was electrically floated with 250 W of power applied to the filament. The temperature of the tungsten filament was estimated to be in the range 1100 to 1500 °C. The external cell wall temperature was about 700 °C. The cell was operated with and without an ultrapure hydrogen flow rate of 5.5 sccm maintained at 300 mTorr.

The rt-plasma phenomena was also studied for cesium metal with hydrogen versus additional controls. The quartz cell was operated under the same conditions as for the Group I nitrates with 1.) hydrogen, argon, neon, and helium alone; 2.) sodium, magnesium, barium, and cesium metals alone, and 3.) sodium, magnesium, barium, and cesium with hydrogen. The pure elements of sodium, magnesium, barium, and cesium were placed in the bottom of the cell and vaporized by filament heating.

The VUV spectrometer was a normal incidence 0.2 meter monochromator equipped with a 1200 lines/mm holographic grating with a platinum coating that covered the region 20–5600 Å. The VUV spectrum was recorded with a CEM. The wavelength resolution was about 0.2 Å (FWHM) with slit widths of 50  $\mu m$ . The increment was 2 Å and the dwell time was 500 ms. The VUV spectrum (900–1300 Å) of the rt-

plasma cell emission was recorded at about the point of the maximum Lyman  $\alpha$  emission to confirm the rt-plasma before the line broadening and high resolution visible spectrum in the region of 4070 Å were recorded.

In addition, regions of the VUV, ultraviolet (UV) and visible (VIS) spectra (400–5600 Å) were recorded with the normal incidence VUV spectrometer using a PMT and a sodium salicylate scintillator to record emission from the atoms and ions of rt-plasma catalysts. The emission was compared with a standard VUV emission spectrum of potassium that was obtained with a gas discharge cell comprised a five-way stainless steel cross that served as the anode with a hollow stainless steel cathode that was coated with  $KNO_3$ ,  $RbNO_3$ , or  $CsNO_3$  by the same procedure used to coat the titanium dissociator. The five-way cross was pressurized with 1 torr of hydrogen to initiate the discharge. The hydrogen was then evacuated so that only catalyst lines were observed. The DC voltage at the time the spectra were recorded was 300 V.

The electron temperatures  $T_e$  of the  $RbNO_3$  and  $KNO_3$  cells were measured from the ratio of the intensity of the  $Rb^+$  741.4 Å line to that of the  $Rb^{2+}$  815.3 Å line and the ratio of the  $K^+$  612.6 Å line to that of the  $K^{2+}$  546.1 Å line, respectively, as described by Griem [15].

The plasma emission from a hydrogen microwave discharge [14] control and each rt-plasma maintained in the filament heated cell was fiber-optically coupled to a high resolution visible spectrometer capable of a resolution of  $\pm 0.06$  Å. The slits were set to 20  $\mu m$ , the step size was 0.1 Å, and the spectra (4000–4090 Å and 6560–6570 Å) were recorded by a PMT in a single accumulation with a 1 second integration time.

To measure the absolute intensity, the high resolution visible spectrometer and detection system were calibrated [16] with 5460.8 Å, 5799.6 Å, and 6965.4 Å light from a Hg-Ar lamp (Ocean Optics, model HG-1) that was calibrated with a NIST certified silicon photodiode. The population density of the  $n=3$  hydrogen excited state  $n_3$  was determined from the absolute intensity of the Balmer  $\alpha$  (6562.8 Å) line measured using the calibrated spectrometer.

### 3. Results and discussion

#### A. Measurement of hydrogen ion temperature and number density from Balmer line broadening

The method of Videnovic et al. [17] was used to calculate the energetic hydrogen atom densities and energies from the width of the 6563 Å Balmer  $\alpha$  line emitted from microwave and rt-plasmas. The full half-width  $\Delta\lambda_G$  of each Gaussian results from the Doppler ( $\Delta\lambda_D$ ) and instrumental ( $\Delta\lambda_I$ ) half-widths:

$$\Delta\lambda_G = \sqrt{\Delta\lambda_D^2 + \Delta\lambda_I^2} \quad (1)$$

$\Delta\lambda_I$  in our experiments was 0.06 Å. The temperature was calculated from the Doppler half-width using the formula:

$$\Delta\lambda_D = 7.16 \times 10^{-6} \lambda_0 \left( \frac{T}{\mu} \right)^{1/2} \text{ (Å)} \quad (2)$$

where  $\lambda_0$  is the line wavelength in Å,  $T$  is the temperature in K ( $1 \text{ eV} = 11,605 \text{ K}$ ), and  $\mu$  is the molecular weight ( $=1$  for hydrogen). In each case, the average Doppler half-width that was not appreciably changed with pressure varied by  $\pm 5\%$  corresponding to an error in the energy of  $\pm 5\%$ . The corresponding number densities for noble gas-hydrogen mixtures varied by  $\pm 20\%$  depending on the pressure.

The results of the 6563 Å Balmer  $\alpha$  line width measured with the high resolution ( $\pm 0.06 \text{ Å}$ ) visible spectrometer on light emitted from rt-plasmas of hydrogen with  $\text{KNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$  are shown in Figures 2-4, respectively. Significant line broadening of 18, 12, and 12 eV and atom densities of  $4 \times 10^{11}$ ,  $6 \times 10^{11}$ , and  $4 \times 10^{11} \text{ atoms/cm}^3$  were observed from a rt-plasma of hydrogen with  $\text{KNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$ , respectively, as shown in Table 1. A hydrogen microwave plasma maintained at the same total pressure showed no excessive broadening corresponding to an average hydrogen atom temperature of  $\approx 3 \text{ eV}$  and a density of  $2 \times 10^{11} \text{ atoms/cm}^3$ . These results could not be explained by Stark or thermal broadening or electric field acceleration of charged species since the measured field of the incandescent heater was extremely weak, 1 V/cm, corresponding to a broadening of much less than 1 eV.

## B. rt-plasma catalyst emission

The VUV spectrum (450–800 Å) of the emission of the  $KNO_3$ - $H_2$  gas cell is shown in Figure 5. The lines of  $K^+$ ,  $K^{2+}$ , and  $K^{3+}$  corresponding to the two possible catalytic reactions were observed as reported previously [18] with the assignments confirmed by a standard potassium plasma spectrum and NIST tables [19-20]. Line emission corresponding to  $K^{3+}$  was observed at 650-670 Å and 740-760 Å.  $K^{2+}$  was observed at 510 Å and 550 Å, and  $K^+$  was observed at 620 Å. A large  $K^{3+}$  peak was also observed at 892 Å.  $K$  was observed at 3447 Å, 4965 Å, and 5084 Å.

The VUV spectrum (500–900 Å) of the emission of the  $RbNO_3$ - $H_2$  gas cell (top curve) and the standard rubidium discharge plasma (bottom curve) are shown in Figure 6. The standard rubidium discharge spectrum according to Sec. 2 is exemplary of the light source used to confirm the line assignments of each of the Group I nitrates studied. Line emission corresponding to  $Rb^{2+}$  was observed at 815.9 Å, 591 Å, 581 Å, 556 Å, and 533 Å.  $Rb^+$  was observed at 741.5 Å, 711 Å, 697 Å, and 643.8 Å. The assignments of the  $Rb^{2+}$  and  $Rb^+$  lines were confirmed by the NIST tables [20].

The UV spectrum (3400–4150 Å) of the emission of the  $CsNO_3$ - $H_2$  gas cell is shown in Figure 7. Line emission corresponding to  $Cs^{2+}$  was observed at 3477 Å, 3618 Å, and 4001 Å.  $Cs^+$  was observed at 3680 Å, 3806 Å, and 4069 Å.  $Cs$  was observed at 3888 Å. The assignments of the  $Cs^{2+}$ ,  $Cs^+$ , and  $Cs$  lines were confirmed by a standard cesium plasma spectrum and the NIST tables [20].

No plasma and no emission except blackbody radiation at long wavelengths was observed for 1.) hydrogen, argon, neon, and helium alone; 2.) sodium, magnesium, barium, and cesium metals alone, and 3.) sodium, magnesium, and barium, with hydrogen; whereas, a bright plasma with strong VUV emission was observed in the case of cesium metal with flowing hydrogen. The VUV spectrum (400–800 Å) of the emission of the  $CsNO_3$ - $H_2$  gas cell is shown in Figure 8. Line emission corresponding to the second ionization energy of cesium, 23.15745 eV [12], for the decay transition  $Cs^{2+}$  to  $Cs^+$  was observed at 533 Å. (The 533 Å emission shown in Figure 8 is actually significantly larger than shown due to the low grating efficiency at the short wavelengths.) The only

cesium lines observed for the standard cesium microwave plasma were in the visible region and no lines were observed at wavelengths shorter than 800 Å in the case of the standard hydrogen microwave plasma.

The resonance lines of Cs II were observed with a sliding spark on the 10.7 m normal incidence vacuum spectrometer at the National Bureau of Standards (NBS) [21] as given in Table 2. The 533 Å emission of the hydrogen catalysis reaction with cesium shown in Figure 8 is dramatically different from the NBS standard cesium spectrum wherein a series of lines of  $Cs^+$  was observed that vanished at the limit of the ionization energy of  $Cs^+$  to  $Cs^{2+}$ . In fact, the ionization limit was not observed; rather, it was derived by NBS to be 23.17(4) eV [21]. Furthermore, I. S. Aleksakhin et al. recorded the emission of cesium in the 45-75 nm region during electron-atom collisions [22]. The ionization energy limit at 533 Å was not observed by I. S. Aleksakhin et al. either.

Atomic hydrogen may resonantly transfer energy to cesium to cause its double ionization to  $Cs^{2+}$ . Considering broadening by the thermal energies, the net enthalpy may be 27.2 eV, a match with the potential energy of atomic hydrogen; thus, it forms an rt-plasma.  $Cs^{2+}$  may then decay and emit the radiation. The vacuum reaction is



Following the resonant transfer, the decay energy for the transition  $Cs^{2+}$  to  $Cs^+$  is predicted to give 23.2 eV (533 Å) line emission corresponding to the second ionization energy of cesium, 23.15745 eV. This line emission was observed as shown in Figure 8 without the Rydberg series of lines of  $Cs^+$  as observed by NBS with a sliding spark method [21] as shown in Table 2. The observed  $Cs^{2+}$  single line emission at 533 Å supports the resonant energy transfer of 27.2 eV from atomic hydrogen to atomic cesium to form an rt-plasma.

### C. Hydrogen Lyman series emission

The VUV spectra (900–1300 Å) of the cell emission recorded at about the point of the maximum Lyman  $\alpha$  emission from the  $KNO_3$ ,  $RbNO_3$ , and  $CsNO_3$  gas cells are shown in Figures 9-11, respectively, with the superimposed spectrum from the hydrogen microwave plasma. Strong Lyman series VUV emission was observed only with  $KNO_3$ ,  $RbNO_3$ , or



$CsNO_3$  (or cesium metal) and hydrogen. The  $CsNO_3$  emission was similar to that of the hydrogen microwave plasma; whereas, the Lyman series lines of the  $KNO_3$  and  $RbNO_3$  rt-plasmas showed population inversion with much greater intensity of atomic hydrogen versus molecular hydrogen compared to the microwave plasma emission.

The population density of the excited hydrogen atoms  $N_\alpha$ ,  $N_\beta$ , and  $N_\gamma$  with principal quantum numbers  $n=2,3$ , and 4, respectively, were obtained from their intensity integrated over the spectral peaks corrected by their Einstein coefficients. The population ratios,  $\frac{N_\beta}{N_\alpha}$  and  $\frac{N_\gamma}{N_\alpha}$ , for pure  $H_2$  and  $H_2$  with  $KNO_3$  or  $RbNO_3$  are given in Table 3.

The important parameter for a lasing medium is the reduced population density  $\frac{N}{g}$  given by the population density  $N$  divided by the statistical weight  $g$  as discussed by Akatsuka et al. [6]. The ratio of  $\frac{N}{g}$  for  $L_\beta$  to  $L_\alpha$  and  $L_\gamma$  to  $L_\alpha$  given in Table 4 demonstrate that with appropriate cavity length and mirror reflection coefficient cw laser oscillations may be obtained between  $n=3$  and  $n=2$  since the corresponding  $\frac{N_\beta g_\alpha}{N_\alpha g_\beta} > 1$  [6]. For the plasma conditions of this experiment ( $T_e \approx 0.7-0.8$  eV,  $n_e \approx 10^{11}$  cm $^{-3}$ ), a threshold reduced overpopulation of  $4.4 \times 10^6$  cm $^{-3}$  is required for lasing assuming a cavity length of 100 cm and a mirror reflection coefficient of 0.99. Modeling results based on the collisional-radiative model [6] given in Sec. 3D show that the threshold condition is achievable for these plasmas. Due to the short lifetime of the Balmer  $\alpha$  line, an exceptionally monochromatic laser with the possibility of fast switching is anticipated.

In a non-recombining plasma [6], thermal electron collisional mechanisms can not produce the conditions necessary for population inversion. All known sources of excitation were exhausted [23]. The observation, then, of population inversion indicates the presence of free energy in the system. This is further evidence that a new chemical source of energy, greater than 12 eV/atom was present. The only possibility known to the authors is the proposed rt-plasma reaction [7].

$T_e$  was determined to be 0.84 eV and 0.76 eV for the  $K^+$  and  $Rb^+$  rt-

plasma respectively. Similarly,  $k_B T_e = (0.30 - 0.43) \text{ eV}$  was determined for a  $K^+$  rt-plasma as reported by Conrads et al. [23], with the assumption of a Maxwell Boltzmann distribution of the level population, and a slightly higher temperature of  $k_B T_e = (0.32 - 0.48) \text{ eV}$  was found when a corona model was applied. The data indicated that the electron temperature was not higher than  $k_B T_e = 0.5 \text{ eV}$ . On this basis, it was astonishing that a strong Lyman beta transition appeared in the spectra since an excitation energy of  $12.1 \text{ eV}$  is required. This energy is a factor of about 25 above the measured thermal energy. The amount of electrons in the Maxwell tail that had enough energy to enhance the Lyman transition was 11 orders of magnitude lower than the total number of electrons. Longer range fields (of the order of mm) were only about a  $1 \text{ V/cm}$ . In addition to electron collisional excitation, known chemical reactions, resonant photon transfer, and multiphoton absorption, and the lowering of the ionization and excitation energies by the state of "non ideality" in dense plasmas were also rejected as the source of ionization or excitation to form the hydrogen plasma.

A source of energy other than that provided by the electric field or known chemical reactions must be considered. We propose that the plasma formed chemically rather than electrically and that the product of the energetic chemical reaction of atomic hydrogen with potassium or rubidium ions which serve as catalysts as well as reactants are compounds having novel hydride ions reported previously [24]. Prior related studies that support the possibility of a novel reaction of atomic hydrogen which produces a chemically generated or assisted plasma (rt-plasma) and produces novel hydride compounds include VUV spectroscopy [7-8, 13-14, 18, 23-31], characteristic emission from catalysts and the hydride ion products [18, 24, 28-29], lower-energy hydrogen emission [13, 25-27], chemically formed plasmas [7-8, 18, 23-24, 28-31], Balmer  $\alpha$  line broadening [8, 14, 24-26, 32], elevated electron temperature [14, 25-26], anomalous plasma afterglow duration [31], power generation [25-26, 30, 32-33], and analysis of novel chemical compounds [34-35].

The predicted catalyst ion emission was observed from rt-plasmas as presented in Sec. 3B. For example, characteristic emission was observed from  $K^{2+}$  as well as  $K^{3+}$  which confirmed the resonant energy

transfer of  $27.2\text{ eV}$  and  $3 \cdot 27.2\text{ eV}$ , respectively, from atomic hydrogen to the catalyst  $K^+/K^+$  and  $K$ , respectively. With a highly conductive plasma, the voltage of the cell was about 20 V, and the field strength was about 1-2 V/cm which was too low to ionize potassium to  $K^{3+}$  which requires at least  $81.7766\text{ eV}$ . The  $K^{3+}$  lines generated in the incandescently heated cell and due to the catalyst reaction of atomic hydrogen were confirmed by a high voltage discharge and NIST tables [19-20].

Then the inverted population is explained by a further resonance energy transfer from the short-lived highly energetic intermediates formed by the rt-plasma reactions to yield  $H(n>2)$  atoms directly by multipole coupling [25] and fast  $H(n=1)$  atoms. The emission of  $H(n=3)$  from fast  $H(n=1)$  atoms excited by collisions with the background  $H_2$  has been discussed by Radovanov et al. [36]. Formation of  $H^+$  is also predicted which is far from thermal equilibrium in terms of the ion temperature as discussed in Sec. 3C and modeled in Sec. 3D. Akatsuka et al. [6] show that it is characteristic of cold recombining plasmas to have the high lying levels in local thermodynamic equilibrium (LTE); whereas, for the low lying levels, population inversion is obtained when  $T_e$  becomes low with an appropriate electron density as shown by the Saha-Boltzmann equation.

#### D. Level Population Model and Lasing Ability

In order to estimate hydrogen excited state level populations and assess lasing ability, the collisional radiative model [6, 37] is applied to the plasma conditions obtained herein ( $T_e \sim 0.8\text{ eV}$ ,  $n_e \sim 10^{11}\text{ cm}^{-3}$ ). The collisional radiative model explicitly includes all level population and de-population mechanisms for each excited level from every other excited level in the hydrogen atom. Excited level  $n$  is, then, populated by collisional excitation from all lower excited states, and collisional and radiative de-excitation from all higher excited states. De-population explicitly includes collisional and radiative de-excitation to all lower states, and collisional excitation to all higher levels. Independent ionization loss, radiative recombination, and dielectronic recombination are included for all levels as well. A separate balance equation is prescribed for each individual level and is coupled to all other level

equations through the population and de-population terms described above.

In order to close the set of equations, truncation was chosen at  $n=5$ . This is justified by both the experimental observation of no measurable emission from higher lying states and *a posteriori* via the model results indicating a progression of negligibly smaller level densities beyond  $n=3$ . The ground state ( $n=1$ ) level population cannot be determined by this method since the important affects of dissociation, molecular recombination, and transport are not included. As discussed earlier (Sec. 3A), however, an estimate based on emission line profiles places the total H atom density  $\sim 5 \times 10^{11} \text{ cm}^{-3}$ . Since this is overwhelmingly dominated by the ground state, the assignment  $n_1 = 5 \times 10^{11} \text{ cm}^{-3}$  will be made throughout.

Solution to the  $n=2 - 5$  level equations under these conditions shows no inversion in any of the level populations. This is an expected result for a steady, thermal plasma. Also, as expected, the dominant mechanisms are found to be population by collisional excitation and de-population by radiative decay.

The results of this calculation ( $n_{2-5} < 10^4 \text{ cm}^{-3}$ ) are inconsistent with the spectroscopic observations. Absolutely calibrating the monochromator near  $H_\alpha$  however yields,  $n_3 \sim 1.25 \times 10^8 \text{ cm}^{-3}$ . There is, then, a heretofore undetermined mechanism providing direct excited state population, *i.e.* pumping. To help quantify the affects of this mechanism, the level equations are once again evaluated with  $n_3$  fixed to  $1.25 \times 10^8 \text{ cm}^{-3}$  and the inclusion of an independent pumping rate. Since spectroscopic results indicate  $n=3 - 2$  inversion, pumping is prescribed to the  $n=3$  state from the ground state,  $n=1$ . The results from this calculation for  $n=1 - 5$  are summarized in Table 5.

Now collisional mechanisms from the  $n=3$  state as well as ground state collisional excitation and radiative decay significantly contribute to population and de-population rates. In addition, a demonstrated inversion in the population between the  $n=3$  and 2 states is predicted. The reduced overpopulation density for this case is  $D(n/g) \sim 4.7 \times 10^6 \text{ cm}^{-3}$ , slightly above the threshold of  $4.4 \times 10^6 \text{ cm}^{-3}$ . The pumping rate is also determined in this analysis yielding a rate of  $\sim 6.44 \times 10^{16} \text{ cm}^{-3} \text{ s}^{-1}$ . Since the  $n=3$  state has a excitation energy of  $12.08 \text{ eV}$ , the pumping mechanism consumes energy at a rate of  $\sim 0.124 \text{ W} \cdot \text{cm}^{-3}$ , which is returned as  $H_\alpha$  and

$H_\beta$  radiation.

#### 4. Conclusion

$2K^+$  to  $K+K^{2+}$ ,  $Rb^+$  to  $Rb^{2+}$ , and  $Cs$  to  $Cs^{2+}$  each provide a reaction with a net enthalpy equal to the potential energy of atomic hydrogen,  $27.2\text{ eV}$ , and  $K$  to  $K^{3+}$  provides a reaction with a net enthalpy equal to  $3 \cdot 27.2\text{ eV}$ . The presence of these gaseous atoms and ions with thermally dissociated hydrogen formed a plasma having strong VUV emission. Emission was observed from  $Rb^+$ ,  $Rb^{2+}$ ,  $K$ ,  $K^+$ ,  $K^{2+}$ ,  $K^{3+}$ ,  $Cs$ ,  $Cs^+$ , and  $Cs^{2+}$  that confirmed the resonant energy transfer with the formation of the corresponding rt-plasma. Emission was also observed from a continuum state of  $Cs^{2+}$  at  $533\text{ \AA}$ . The single emission feature with the absence of the other corresponding Rydberg series of lines from species confirmed the resonant energy transfer of  $27.2\text{ eV}$  from atomic hydrogen to atomic cesium.

A stationary inverted Lyman population was observed with potassium and rubidium catalysts. The ionization and population of excited atomic hydrogen levels was attributed to energy provided by the rt-plasma reactions. The high ion temperature with a relatively low electron temperature,  $T_e < 1\text{ eV}$ , were characteristic of cold recombining plasmas [6]. These conditions of the rt-plasmas favored an inverted population in the lower levels. Thus, the catalysis of atomic hydrogen may pump a cw HI laser. From our results, laser oscillations are expected between  $n=3$  and  $n=2$ .

#### References

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Table 1. Energetic hydrogen atom densities and energies for rt-plasmas determined from the 6563 Å Balmer  $\alpha$  line width.

Plasma Gas	Hydrogen Atom Density <sup>a</sup> ( $10^{11}$ atoms/cm <sup>3</sup> )	Hydrogen Atom Energy <sup>b</sup> (eV)
$H_2$	2	2-3 <sup>c</sup>
$K; K^+ / K^+ / H_2$	4	15-18
$Rb^+ / H_2$	6	9-12
$Cs / H_2$	4	10-12

<sup>a</sup> Approximate Calculated after [17].

<sup>b</sup> Calculated after [17].

<sup>c</sup> Measured on a microwave discharge after [14].

Table 2. Resonance lines of Cs II observed with a sliding spark on the 10.7 m normal incidence vacuum spectrometer at NBS [21]. The uncertainty of the wavelengths is  $\pm 0.005$  Å.

$\lambda$ (Å)	Intensity	$\sigma$ (cm <sup>-1</sup> )	Upper Level
926.657	40000	107914.8	$6p^6 5d^3 P_1$
901.270	35000	110954.5	$6s3/2[3/2]_1$
813.837	15000	122874.7	$6s1/2[1/2]_1$
808.761	15000	123645.9	$5d^3 D_1$
718.138	15000	139249.0	$5d^1 P_1$
668.386	500	149614	$7s3/2[3/2]_1$
657.112	100	152181	$6d^3 P_1$
639.356	2000	156407	$6d^3 D_1$
612.756	35	163189	$7s1/2[1/2]_1$
591.044	250	169192	$6d^1 P_1$
607.291	50	164666	$8s3/2[3/2]_1$
575.320	10	173816	$6d^3 D_1$
564.158	1	177256	$7d^1 P_1$

Table 3. The population density ratios  $\frac{N_\beta}{N_\alpha}$  and  $\frac{N_\gamma}{N_\alpha}$  for pure  $H_2$ ,  $KNO_3$ , and  $RbNO_3$ .

Plasma Gas	$\frac{N_\beta}{N_\alpha}$	$\frac{N_\gamma}{N_\alpha}$
Pure $H_2$ <sup>a</sup>	0.664	0.521
$KNO_3$	4.72	3.48
$RbNO_3$	4.30	1.26

<sup>a</sup> Measured on microwave discharge maintained after [13-14].

Table 4. The reduced population density ratios  $\frac{N}{g}$  for pure  $H_2$ ,  $KNO_3$ , and  $RbNO_3$ .

Plasma Gas	$\frac{N_\beta}{N_\alpha} \frac{g_\alpha}{g_\beta}$ a	$\frac{N_\gamma}{N_\alpha} \frac{g_\alpha}{g_\gamma}$ b
Pure $H_2$ <sup>c</sup>	0.292	0.130 <sup>c</sup>
$KNO_3$	2.07	0.870
$RbNO_3$	1.89	0.314

a  $\frac{g_\alpha}{g_\beta} = 0.444$  where  $g = 2n^2$  and  $n$  is the principal quantum number

b  $\frac{g_\alpha}{g_\gamma} = 0.250$

<sup>c</sup> Measured on microwave discharge after [14].

Table 5. Level densities  $n_n$  for excited states  $n=1 - 5$  with an  $n=3$  pumping mechanism.

$n$	$n_n(10^8 \text{ cm}^{-3})$
1	5000
2	0.18
3	1.25
4	0.000229
5	0.000138

## Figure Captions

Figure 1. The experimental set up comprising a filament gas cell to form an rt-plasma light source and an VUV spectrometer which was differentially pumped.

Figure 2. The 6563 Å Balmer  $\alpha$  line width recorded with a high resolution ( $\pm 0.06$  Å) visible spectrometer on an rt-plasma formed with  $K$  and  $K^+/K^+$  catalysts. Significant broadening was observed corresponding to an average hydrogen atom temperature of 18 eV.

Figure 3. The 6563 Å Balmer  $\alpha$  line width recorded with a high resolution ( $\pm 0.06$  Å) visible spectrometer on an rt-plasma formed with  $Rb^+$  catalyst. Significant broadening was observed corresponding to an average hydrogen atom temperature of 12 eV.

Figure 4. The 6563 Å Balmer  $\alpha$  line width recorded with a high resolution ( $\pm 0.06$  Å) visible spectrometer on an rt-plasma formed with  $Cs$  catalyst. Significant broadening was observed corresponding to an average hydrogen atom temperature of 12 eV.

Figure 5. The VUV spectrum (450–800 Å) of the cell emission recorded at about the point of the maximum Lyman  $\alpha$  emission from a gas cell at a cell temperature of 700 °C comprising a tungsten filament, a titanium dissociator, 300 mtorr hydrogen, and vaporized  $K$  and  $K^+$  from  $KNO_3$  that was recorded with a CEM. Line emission corresponding to  $K^{3+}$  was observed at 650–670 Å and 740–760 Å.  $K^{2+}$  was observed at 510 Å and 550 Å, and  $K^+$  was observed at 620 Å.

Figure 6. The VUV spectrum (500–900 Å) of the emission of the  $RbNO_3$ - $H_2$  gas cell (top curve) and the standard rubidium plasma (bottom curve). The  $RbNO_3$ - $H_2$  gas cell comprised a tungsten filament, a titanium dissociator, 300 mTorr hydrogen, and vaporized  $Rb^+$  from  $RbNO_3$ . The emission was recorded with a CEM at about the point of the maximum Lyman  $\alpha$  at a cell temperature of 700 °C. Line emission corresponding to  $Rb^{2+}$  was observed at 815.9 Å, 591 Å, 581 Å, 556 Å, and 533 Å.  $Rb^+$  was observed at 741.5 Å, 711 Å, 697 Å, and 643.8 Å.

Figure 7. The UV spectrum (3400–4150 Å) the cell emission recorded at about the point of the maximum Lyman  $\alpha$  emission from a gas cell at a cell temperature of 700 °C comprising a tungsten filament, a titanium dissociator, 300 mtorr hydrogen, and vaporized  $Cs$  from  $CsNO_3$ .

that was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator. Line emission corresponding to  $Cs^{2+}$  was observed at 3477 Å, 3618 Å, and 4001 Å.  $Cs^+$  was observed at 3680 Å, 3806 Å, and 4069 Å.  $Cs$  was observed at 3888 Å.

Figure 8. The VUV spectrum (400–800 Å) of the cell emission from the gas cell at a cell temperature of 700 °C comprising a tungsten filament, vaporized cesium metal, and 300 mtorr hydrogen that was recorded with a PMT and a sodium salicylate scintillator. Emission was observed from a continuum state of  $Cs^{2+}$  at 533 Å. The single emission feature with the absence of the other corresponding Rydberg series of lines from  $Cs^+$  confirmed the resonant energy transfer of 27.2 eV from atomic hydrogen to atomic cesium.

Figure 9. The VUV spectra (900–1300 Å) of the cell emission from hydrogen microwave plasma (dotted line) and the  $KNO_3$ - $H_2$  rt-plasma (solid line) with an inverted Lyman population.

Figure 10. The VUV spectra (900–1300 Å) of the cell emission from hydrogen microwave plasma (dotted line) and the  $RbNO_3$ - $H_2$  rt-plasma (solid line) with an inverted Lyman population.

Figure 11. The VUV spectra (900–1300 Å) of the cell emission from hydrogen microwave plasma (dotted line) and the  $CsNO_3$ - $H_2$  rt-plasma (solid line) with no inverted Lyman population.

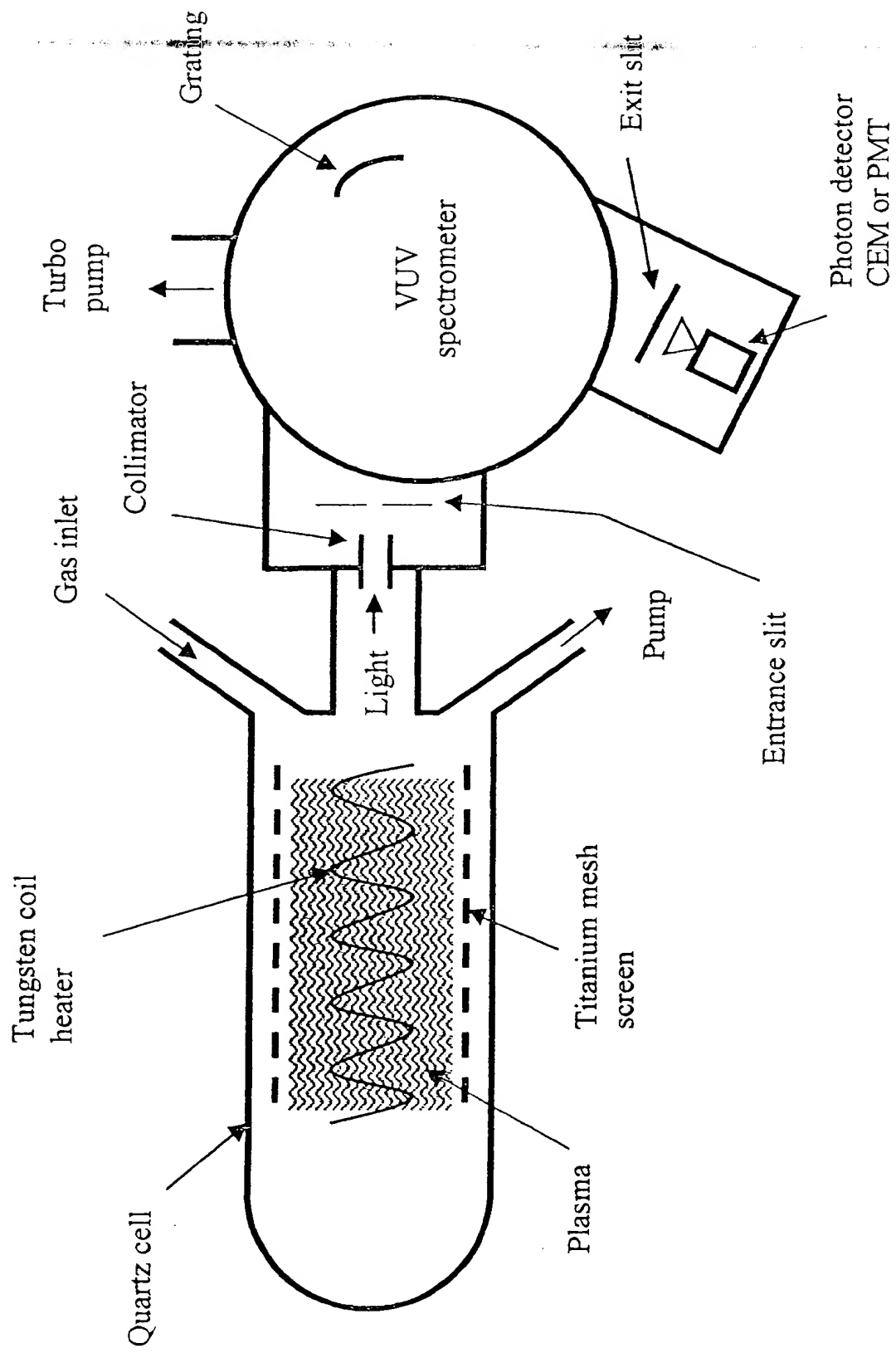


Fig. 1



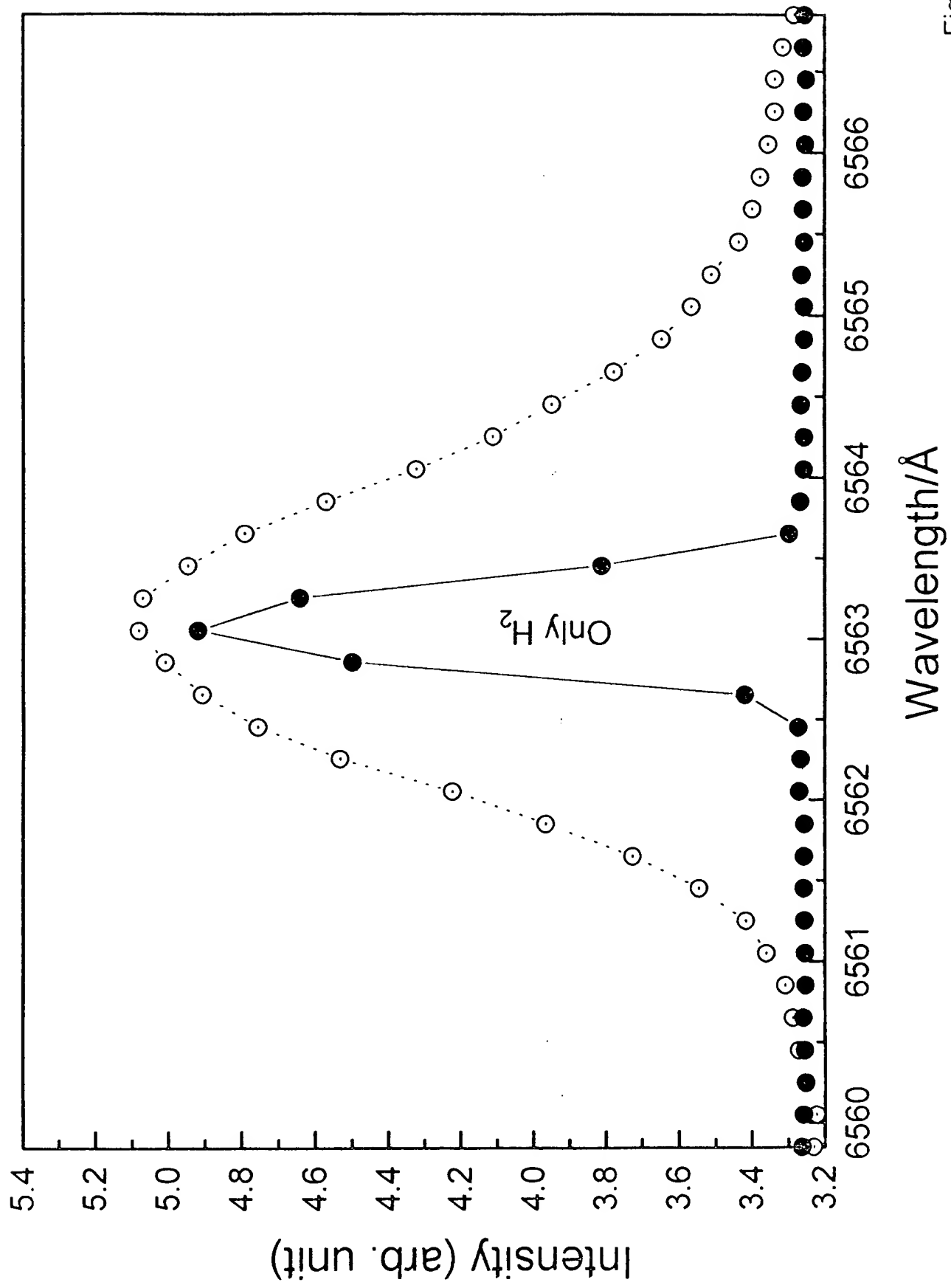


Fig. 2

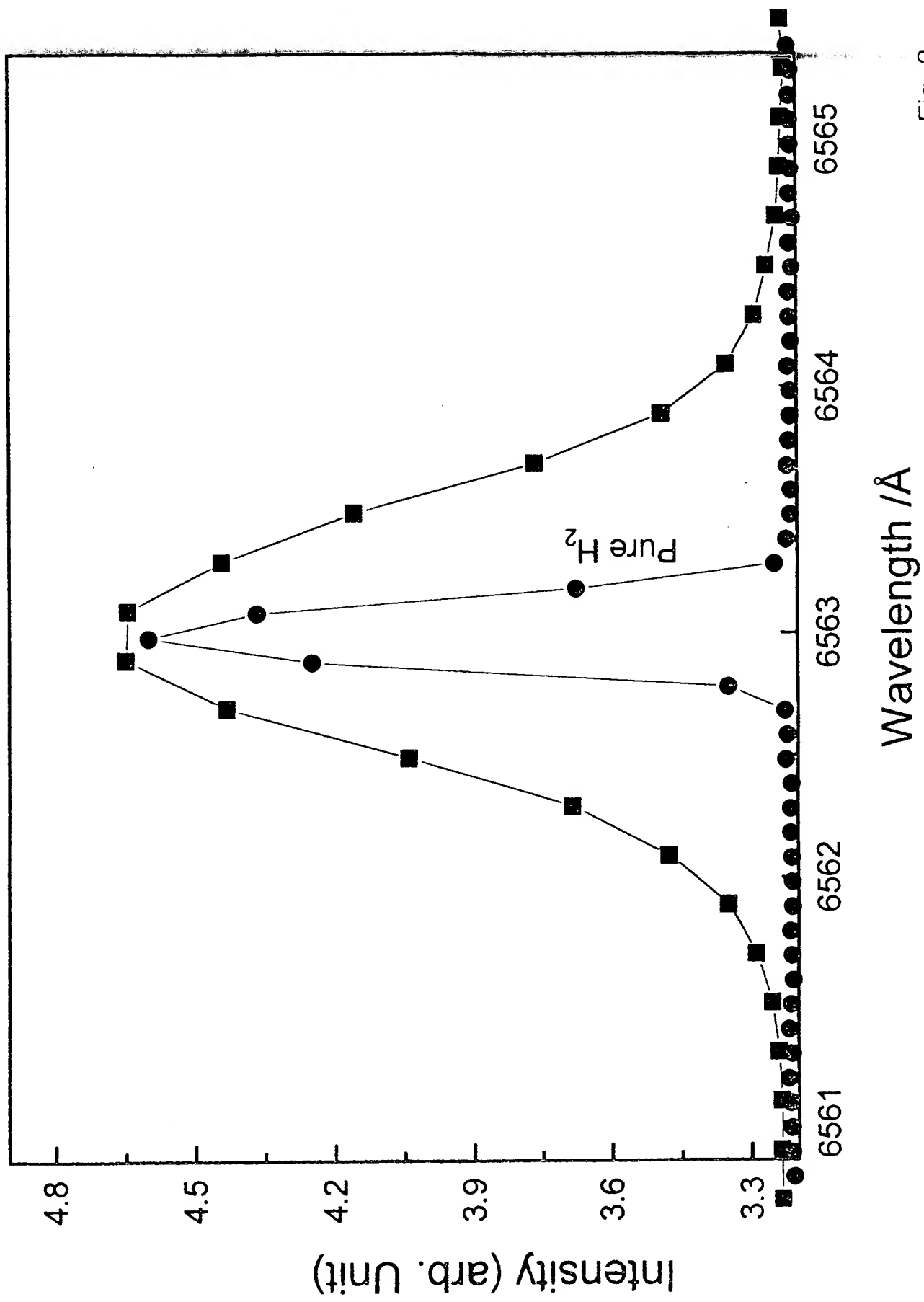
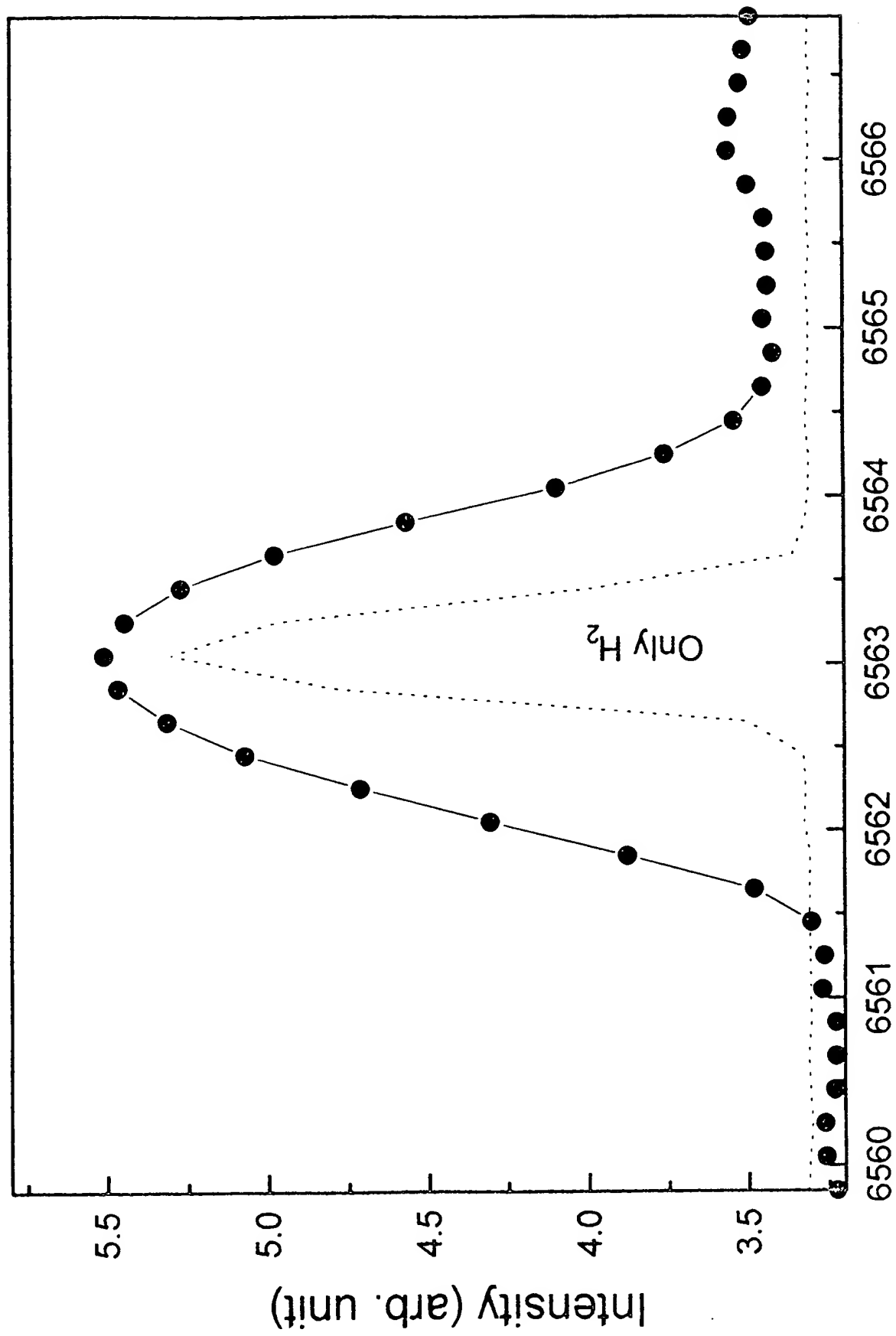


Fig. 3



Wavelength/Å

Fig. 4

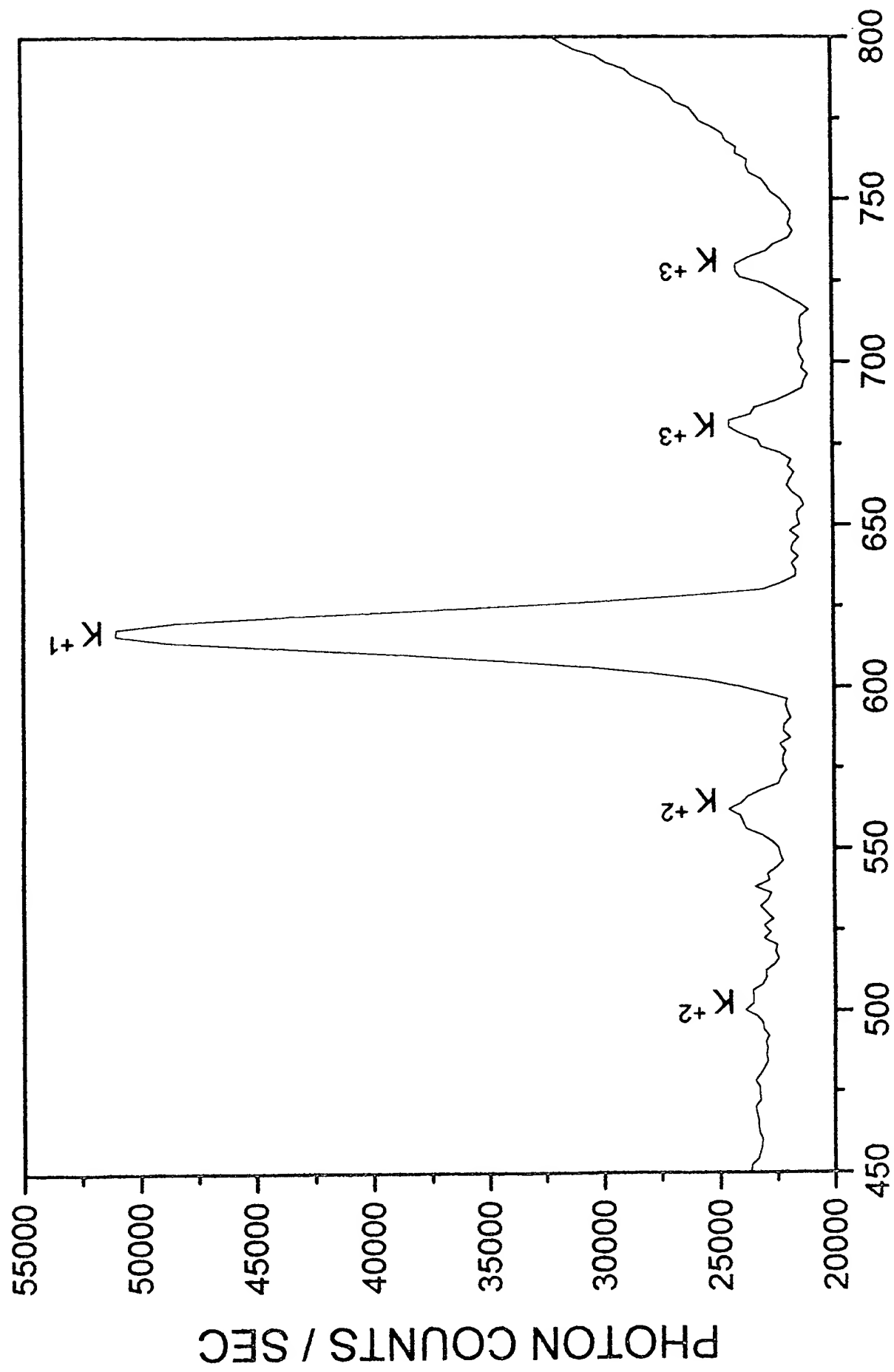
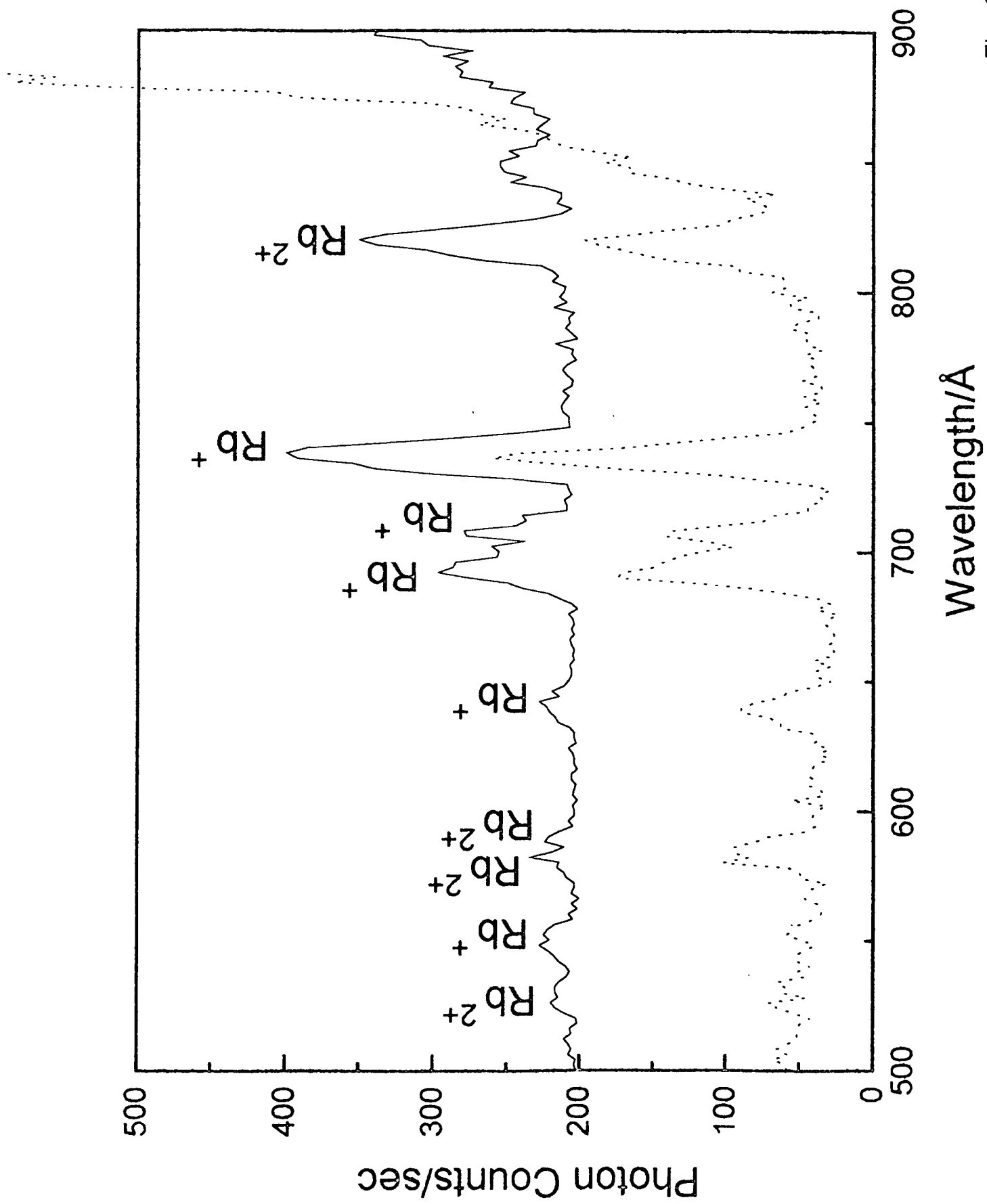
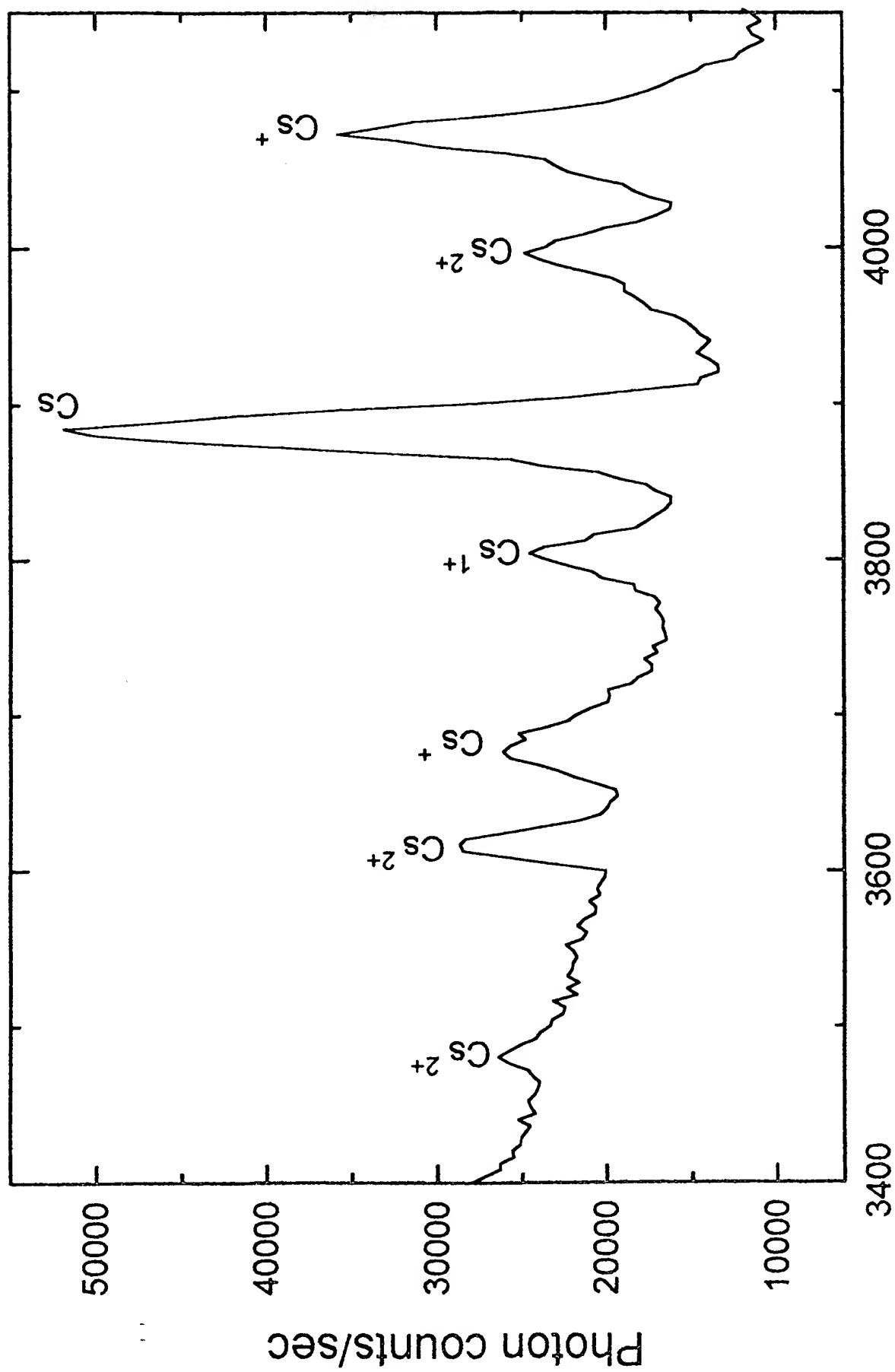


Fig. 5

Fig. 6





Wavelength/Å

Fig. 7

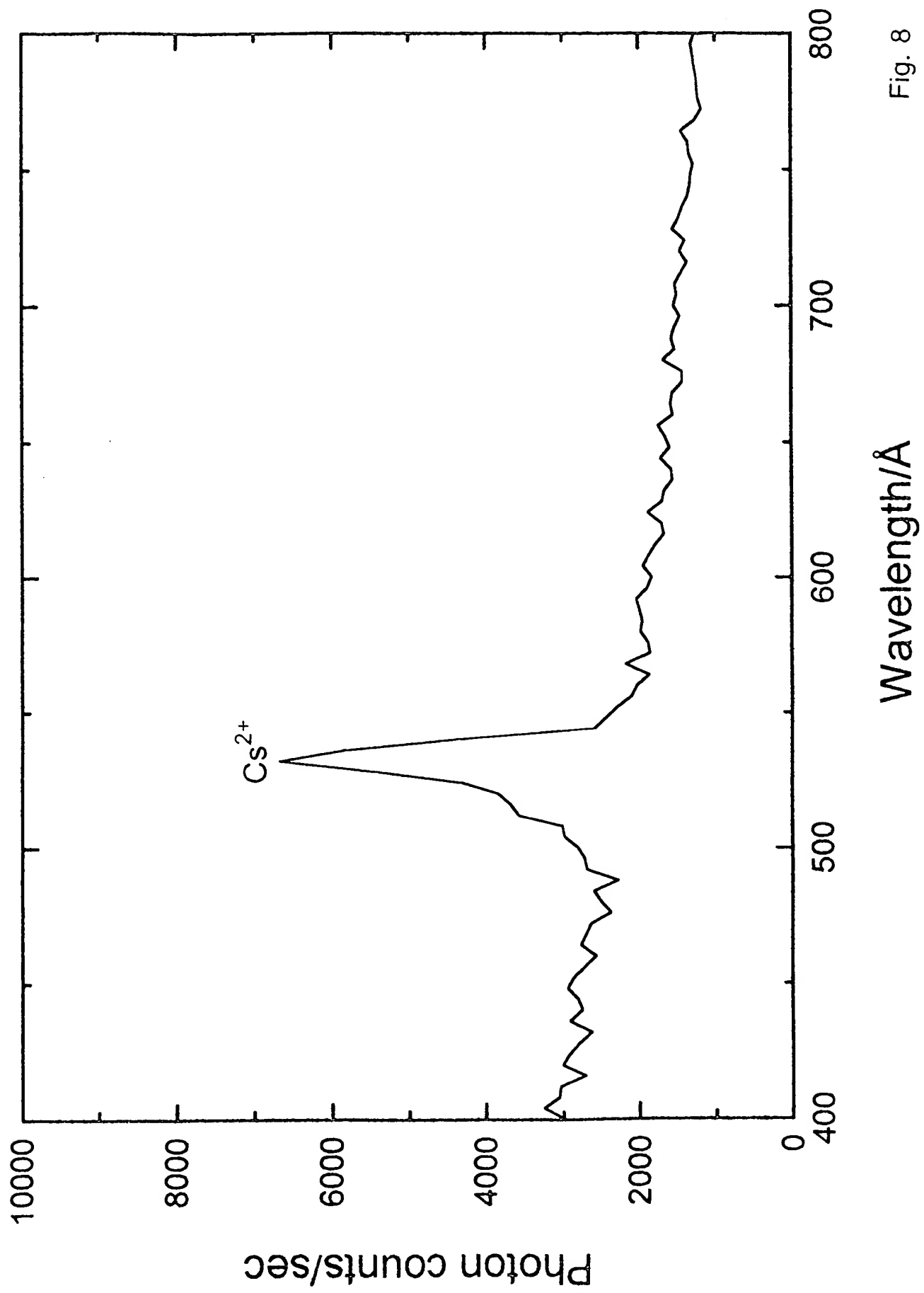


Fig. 8

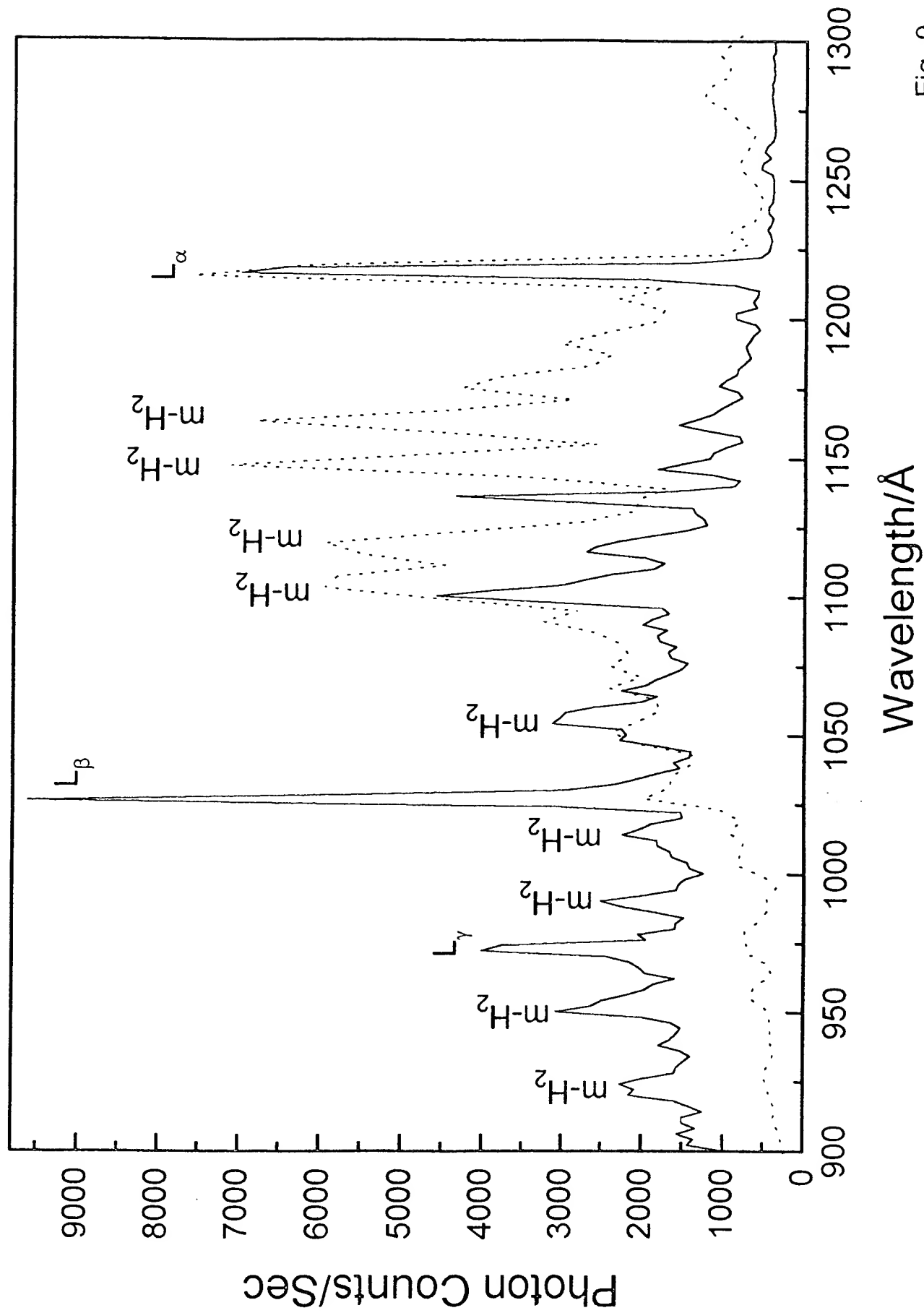


Fig. 9



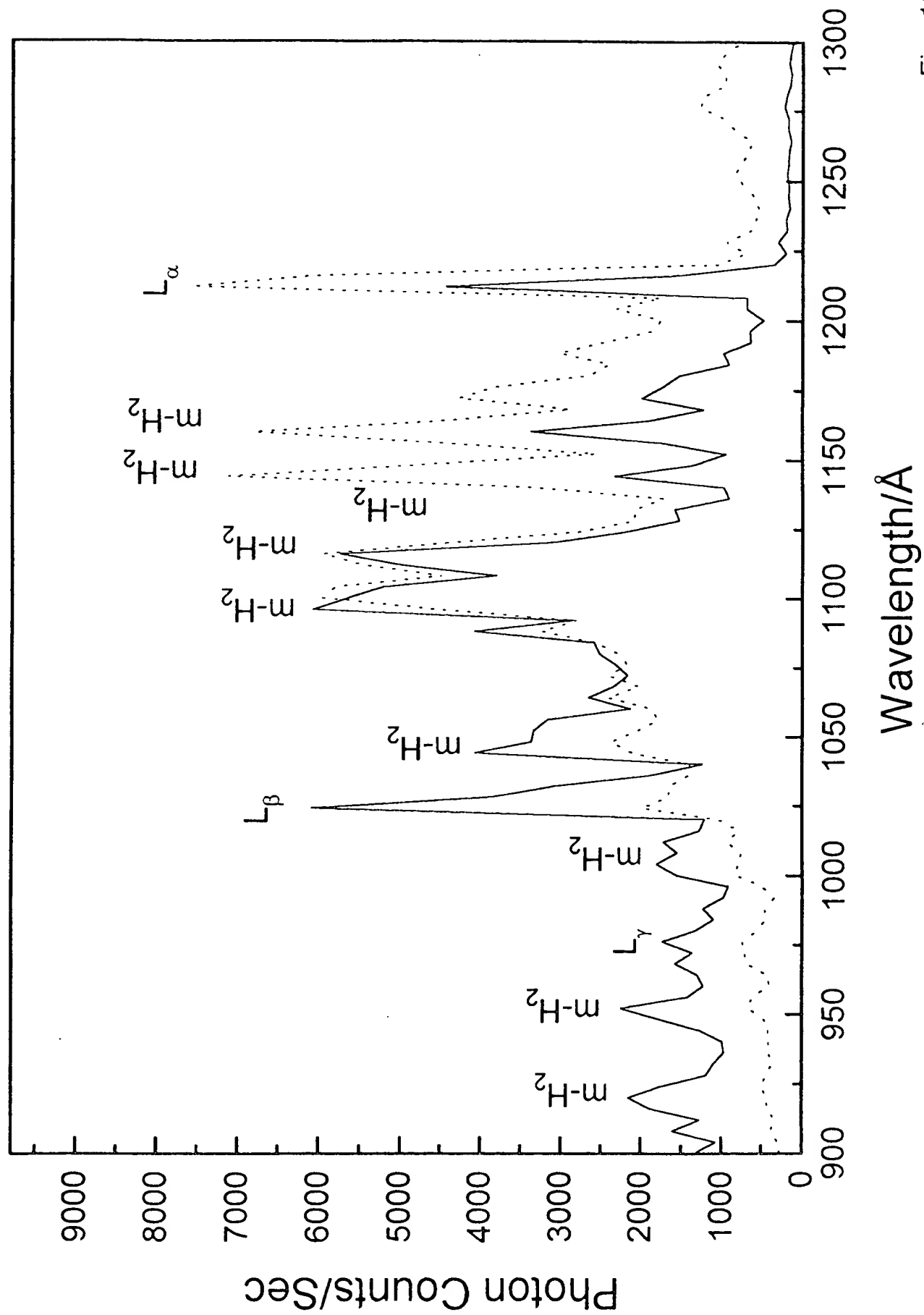


Fig. 10

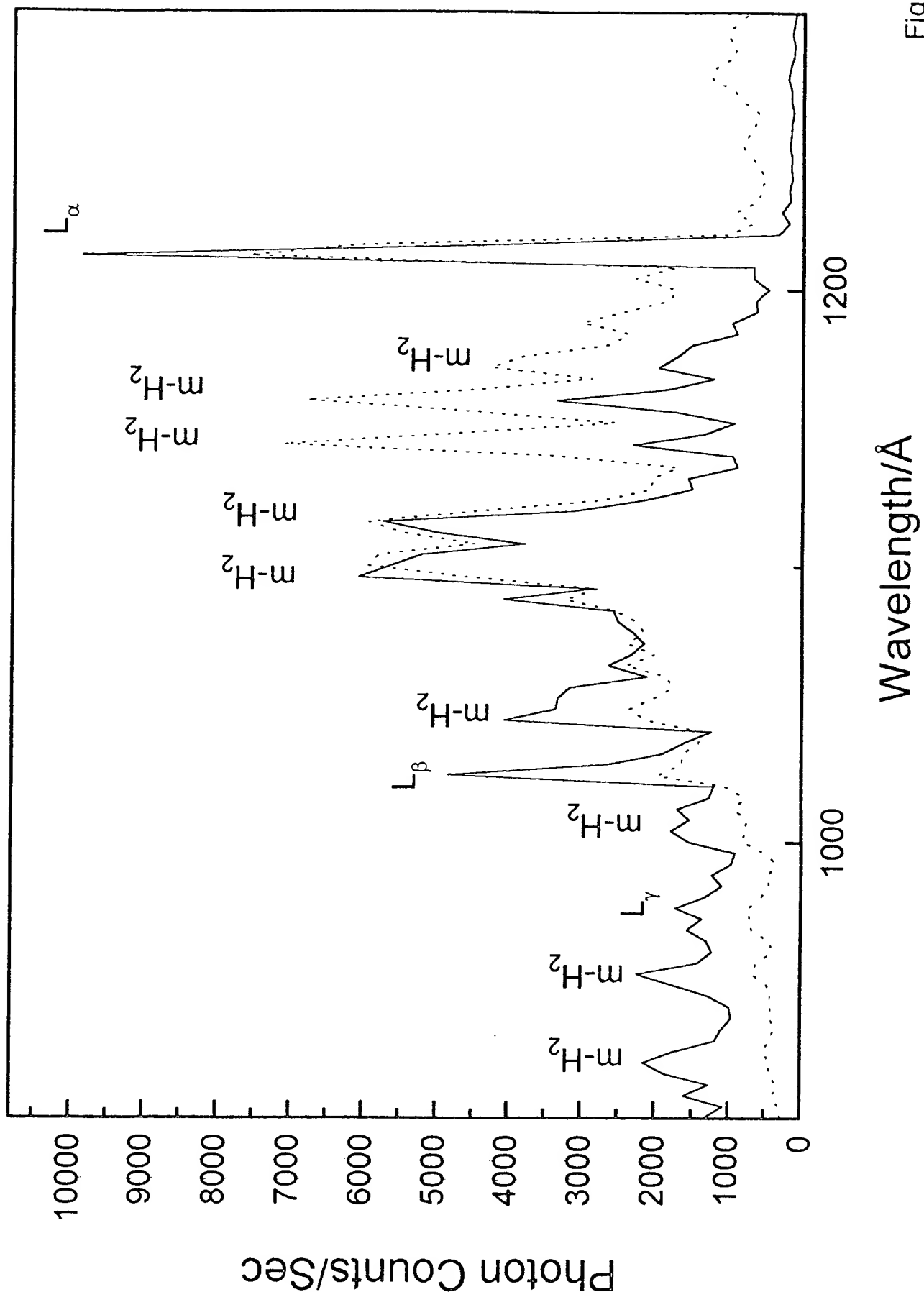


Fig. 11